

Relativistic coupled-cluster study of RaF as a candidate for parity and time reversal violating interaction

Sudip Sasmal,^{1,*} Himadri Pathak,^{1,†} Malaya K. Nayak,^{2,‡} Nayana Vaval,¹ Sourav Pal³

¹*Electronic Structure Theory Group, Physical Chemistry Division,
CSIR-National Chemical Laboratory, Pune, 411008, India*

²*Theoretical Chemistry Section, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India and*

³*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India*

We have employed both Z-vector method and the expectation value approach in the relativistic coupled-cluster framework to calculate the scalar-pseudoscalar (S-PS) \mathcal{P}, \mathcal{T} -odd interaction constant (W_s) and the effective electric field (E_{eff}) experienced by the unpaired electron in the ground electronic state of RaF. Further, the magnetic hyperfine structure constants of ^{223}Ra in RaF and $^{223}\text{Ra}^+$ are also calculated and compared with the experimental values wherever available to judge the extent of accuracy obtained in the employed methods. The outcome of our study reveals that the Z-vector method is superior than the expectation value approach in terms of accuracy obtained for the calculation of ground state property. The Z-vector calculation shows that RaF has a high E_{eff} (52.5 GV/cm) and W_s (141.2 kHz) which makes it a potential candidate for the eEDM experiment.

PACS numbers: 31.15.A-, 31.15.bw, 31.15.vn, 31.30.jp

I. INTRODUCTION

The ongoing accelerator based experiments in the search for new physics can solve some of the unanswered problems of the fundamental physics like matter-antimatter asymmetry. A complementary to these high energy experiments is the search for violation in spatial inversion (\mathcal{P}) and time reversal (\mathcal{T}) symmetries in nuclei, atoms or molecules in the low energy domain using non-accelerator experiments [1–7]. One of such \mathcal{P}, \mathcal{T} -violating interaction results into the electric dipole moment of electron (eEDM) [8–11]. The eEDM predicted by the standard model (SM) of elementary particle physics is too small ($< 10^{-38}$ e cm) [12] to be observed by the today's experiment. However, many extensions of the SM predict the value of eEDM to be in the range of $10^{-26} - 10^{-29}$ e cm [13] and the sensitivity of the modern eEDM experiment also lies in the same range. Till date, the experiment done by ACME collaboration [11] using ThO yields the best upper bound limit of eEDM. The high sensitivity of modern eEDM experiment is mainly due to the fact that heavy paramagnetic diatomic molecules offer a very high internal effective electric field (E_{eff}), which enhances the eEDM effects [14, 15]. In the experiment, both eEDM and the coupling interaction between the scalar-hadronic current and the pseudoscalar electronic current contribute to the \mathcal{P}, \mathcal{T} -odd frequency shift. Therefore, it is impossible to decouple the individual contribution from these two effects in a single experiment. However, it is possible to untwine these two contributions from each other and an independent limit on the value of eEDM (d_e) and scalar-pseudoscalar (S-PS) cou-

pling constant (k_s) can be obtained by using data from two different experiments as suggested by Dzuba *et al* [16]. It is, therefore, an accurate value of the E_{eff} and the scalar-pseudoscalar (S-PS) \mathcal{P}, \mathcal{T} -odd interaction constant (W_s) are needed since these two quantities cannot be measured by means of any experiment. Therefore, one has to rely on an accurate *ab initio* theory that can simultaneously take care of the effects of relativity and electron correlation for the calculation of these quantities.

The best way to include the effects of special relativity in the electronic structure calculations is to solve the Dirac-Hartree-Fock (DHF) equation in the four-component framework. The DHF method considers an average electron-electron interaction and thus misses the correlation between electrons having same spin. On the other hand, the single reference coupled-cluster (SRCC) method is the most preferred many-body theory to incorporate the dynamic part of the electron correlation. The calculation of property in the SRCC framework can be done either numerically or analytically. In numerical method (also known as the finite-field (FF) method), the coupled-cluster amplitudes are functions of the external field parameters [17] and thus, for calculations of each property, separate set of CC calculation is needed. The error associated with the FF method is also dependent on the method of calculation, i.e., the number of data points considered for the numerical differentiation. On the contrary, in the analytical method, the CC amplitudes are independent of the external field of perturbation and therefore, one needs to solve only one set of CC equation for the calculations of any number of properties. Normal CC (NCC) method being non-variational, does not satisfy the generalized Hellmann-Feynman (GHF) theorem and thus, the expectation value and the energy derivative approach are two different formalisms for the calculation of first order property. However, the energy derivative in NCC framework is the corresponding expectation value

*sudipsasmal.chem@gmail.com

†hmdrpthk@gmail.com

‡mk.nayak72@gmail.com

plus some additional terms which make it closer to the property value obtained in the full configuration interaction (FCI) method. Thus, the property value obtained in the energy derivative method is much more reliable than the corresponding expectation value method. Another disadvantage of the expectation value method is that it leads to a non-terminating series and any truncation further introduces an additional error. The Z-vector method [18, 19] (an energy derivative method), on the other hand, leads to a naturally terminating series at any level of approximation. The higher order derivative in the NCC framework can be calculated by using the Lagrange multiplier method [20] and for the first order energy derivative, it leads to the identical equations as of Z-vector method. It is worth to note that there are alternative options like expectation value CC (XCC) [21], unitary CC (UCC) [22], and extended CC (ECC) [23, 24] to solve the SRCC equation. All these methods are known in the literature as the variational coupled-cluster (VCC) method [25]. These VCC methods are well established in the non-relativistic framework but are not that much popular in the relativistic domain, a few are documented in the literature like relativistic UCC by Sur *et al.* [26, 27], applicable only for the purpose of atomic calculations. Recently, Sasmal *et al.* implemented ECC in the four-component relativistic domain to calculate the magnetic hyperfine structure (HFS) constants of both atoms and molecules in their open-shell ground state configuration [28]. The ECC method being variational satisfies the GHF theorem, therefore, expectation value and the energy derivative approach are identical to each other. However, in ECC method amplitude equations for the excitation and de-excitation operators are coupled to each other, whereas, in Z-vector method, the amplitude equations of excitation operator are decoupled from the amplitude equations of the de-excitation operator. This accelerates the convergence in the Z-vector method with a lesser computational cost as compared to the ECC.

In this work, we have calculated the E_{eff} and W_s of RaF in its ground electronic ($^2\Sigma$) state using Z-vector method in the CC framework. We also calculated these properties in the expectation value method to show the superiority of the Z-vector method over the expectation value method. We have chosen the RaF molecule for the following reasons: This molecule has been proposed for the \mathcal{P} -odd and \mathcal{P}, \mathcal{T} -odd experiment [29–31] due to its high Schiff moment, E_{eff} and W_s . The E_{eff} of $^2\Sigma$ state of RaF is even higher than the ground state ($^2\Sigma$) of YbF. Therefore, the more precise value of E_{eff} and W_s and their ratio are very important for the eEDM experiment using this molecule. RaF can be directly laser cooled as it has high diagonal Franck-Condon matrix element between the ground and first excited electronic state and the corresponding transition frequency lies in the visible region with a reasonable lifetime [29].

The manuscript is organized as follows. A brief overview of the expectation value and the Z-vector

method in the CC framework including concise details of the properties calculated in this work are given in Sec. II. Computational details are given in Sec. III. We presented our calculated results and discuss about those in Sec. IV before making concluding remark. Atomic unit is used consistently unless stated.

II. THEORY

A. Expectation value and Z-vector method

The DHF wavefunction is the best description of the ground state in a single determinant theory and thus, it is used as a reference function for the correlation calculations where the Dirac-Coulomb (DC) Hamiltonian is used which is given by

$$H_{DC} = \sum_i \left[-c(\vec{\alpha} \cdot \vec{\nabla})_i + (\beta - \mathbb{1}_4)c^2 + V^{nuc}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \mathbb{1}_4 \right]. \quad (1)$$

Here, α and β are the usual Dirac matrices, c is the speed of light, $\mathbb{1}_4$ is the 4×4 identity matrix and the sum is over all the electrons, which is denoted by i . The Gaussian charge distribution is used as nuclear potential function ($V^{nuc}(r_i)$). The DHF method approximates the electron-electron repulsion in an average way and thus misses the correlation between same spin electrons. In this article, we have used the SRCC method to incorporate the dynamic part of electron correlation. The SRCC wavefunction is given by $|\Psi_{cc}\rangle = e^T |\Phi_0\rangle$, where Φ_0 is the DHF wavefunction and T is coupled-cluster excitation operator which is given by

$$T = T_1 + T_2 + \dots + T_N = \sum_n^N T_n, \quad (2)$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} t_{ij\dots}^{ab\dots} a_a^\dagger a_b^\dagger \dots a_j a_i, \quad (3)$$

where $i,j(a,b)$ are the hole(particle) indices and $t_{ij\dots}^{ab\dots}$ are the cluster amplitudes corresponding to the cluster operator T_m . In coupled-cluster single and double (CCSD) model, $T = T_1 + T_2$. The equations for T_1 and T_2 are given as

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad (4)$$

where H_N is the normal ordered DC Hamiltonian and subscript c means only the connected terms exist in the contraction between H_N and T . Size-extensivity is ensured by this connectedness.

Once the cluster amplitudes are solved, the expectation value of any property operator of interest, $\langle O_N \rangle$ can

be calculated by the following expression as given in Ref. [32],

$$\begin{aligned}\langle O_N \rangle &= \frac{\langle \Psi_{cc} | O_N | \Psi_{cc} \rangle}{\langle \Psi_{cc} | \Psi_{cc} \rangle} = \frac{\langle \Phi_0 e^{T^\dagger} | O_N | e^T \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle} \\ &= \langle \Phi_0 | (e^{T^\dagger} O_N e^T)_c | \Phi_0 \rangle.\end{aligned}\quad (5)$$

The above series is a non-terminating series. Since, the dominant contribution comes from the linear terms, therefore, linear approximation is the most favored choice. The detailed diagrammatic expression consider-

ing only linear terms within the CCSD approximation is given in Fig. 1 and the corresponding algebraic equation is given as in Eq. 6. We have used Einstein summation convention, i.e., the repeated indices are summed over in the expression. The t amplitudes with particle(hole) indices at the subscript(superscript) are the corresponding amplitudes of the T^\dagger operator. It is interesting to note that there is no possible diagrams (as well as algebraic expression) of the kind $T_2^\dagger O$ or OT_2 , since closed connected diagrams can not be constructed by these two expressions.

$$\begin{aligned}\langle O \rangle &= O(i, a) \cdot t_a^i + t_a^i \cdot O(a, i) + t_a^i \cdot O(a, b) \cdot t_b^i - t_a^i \cdot O(j, i) \cdot t_j^a + t_{ab}^{ij} \cdot O(b, j) \cdot t_i^a + \\ &t_a^i \cdot O(j, b) \cdot t_{ij}^{ab} - \frac{1}{2} t_{ab}^{ij} \cdot O(k, j) \cdot t_{ik}^{ab} + \frac{1}{2} t_{ab}^{ij} \cdot O(b, c) \cdot t_{ij}^{ac}.\end{aligned}\quad (6)$$

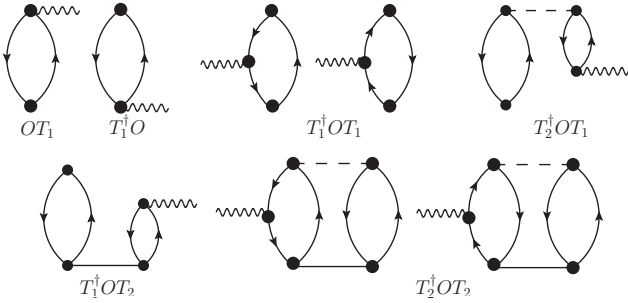


FIG. 1: Diagrams for expectation value approach using linear truncation scheme

The CC amplitudes are solved in a nonvariational way (using Eq. 4) and thus, the CC energy is not minimized with respect to the determinantal coefficient and the molecular orbital coefficient in the expansion of the many electron correlated wavefunction for a fixed nuclear geometry [17]. Therefore, the calculation of CC energy derivative needs to include the derivative of energy with respect to these two coefficients in addition to the derivative of these two parameters with respect to the external field of perturbation. However, the derivative terms associated with determinantal coefficient can be integrated by the introduction of a perturbation independent linear operator, Λ [19]. Λ is an antisymmetrized de-excitation operator whose second quantized form is given by

$$\Lambda = \Lambda_1 + \Lambda_2 + \dots + \Lambda_N = \sum_n \Lambda_n, \quad (7)$$

where

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} \lambda_{ab\dots}^{ij\dots} a_i^\dagger a_j^\dagger \dots a_b a_a, \quad (8)$$

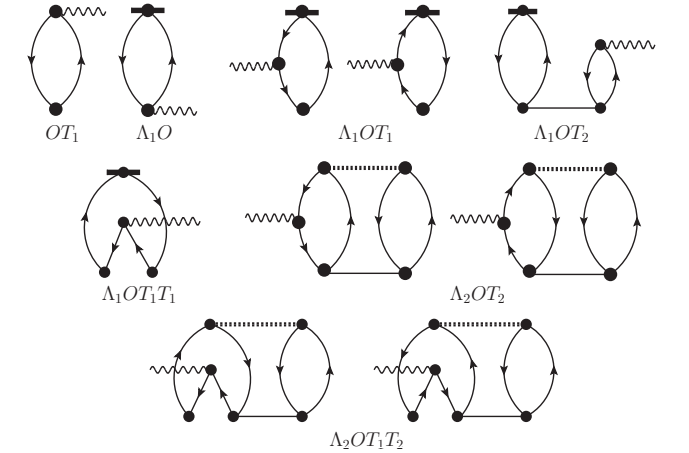


FIG. 2: Diagrams for the energy derivative in Z-vector method

where $\lambda_{ab\dots}^{ij\dots}$ are the cluster amplitudes corresponding to the operator Λ_m . The detailed description of Λ operator and amplitude equation is given in Ref. [19]. In CCSD model, $\Lambda = \Lambda_1 + \Lambda_2$. The explicit equations for the amplitudes of Λ_1 and Λ_2 operators are given by

$$\langle \Phi_0 | [\Lambda(H_N e^T)_c]_c | \Phi_i^a \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle = 0, \quad (9)$$

$$\begin{aligned}\langle \Phi_0 | [\Lambda(H_N e^T)_c]_c | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{ij}^{ab} \rangle \\ + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle \langle \Phi_i^a | \Lambda | \Phi_{ij}^{ab} \rangle = 0.\end{aligned}\quad (10)$$

It is interesting to note that the third term of Eq. 10 is of the nature of disconnected type and it eventually produces one disconnected diagram in the Λ_2 amplitude equation (for details see Ref. [19, 33]). Although the diagram is disconnected but it does not have any closed

part. This ensures that the corresponding energy diagram is linked which restores the size extensivity. The energy derivative can be given as

$$\Delta E' = \langle \Phi_0 | (O_N e^T)_c | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda (O_N e^T)_c]_c | \Phi_0 \rangle \quad (11)$$

where, O_N is the derivative of normal ordered perturbed

$$\begin{aligned} \Delta E' = & O(i, a) \cdot t_i^a + \lambda_a^i \cdot O(a, i) + \lambda_a^i \cdot O(a, b) \cdot t_i^b + \lambda_a^i \cdot O(j, i) \cdot t_j^a + \lambda_a^i \cdot O(j, b) \cdot t_{ij}^{ab} - \lambda_a^i \cdot O(j, b) \cdot t_i^b \cdot t_j^a - \\ & \frac{1}{2} \lambda_{ab}^{ij} \cdot O(k, j) \cdot t_{ik}^{ab} + \frac{1}{2} \lambda_{ab}^{ij} \cdot O(b, c) \cdot t_{ij}^{ac} - \frac{1}{2} \lambda_{bc}^{ik} \cdot O(j, a) \cdot t_i^a \cdot t_{jk}^{bc} - \frac{1}{2} \lambda_{ac}^{jk} \cdot O(i, b) \cdot t_i^a \cdot t_{jk}^{bc}. \end{aligned} \quad (12)$$

B. One electron property operators

The E_{eff} can be obtained by evaluating the following matrix element

$$E_{\text{eff}} = |W_d \Omega| = |\langle \Psi_\Omega | \sum_j^n \frac{H_d(j)}{d_e} | \Psi_\Omega \rangle|, \quad (13)$$

where Ω is the component of total angular momentum along the molecular axis and Ψ_Ω is the wavefunction corresponding to Ω state. n is the total number of electrons and H_d is the interaction Hamiltonian of d_e with internal electric field and is given by [34, 35],

$$H_d = 2icd_e \gamma^0 \gamma^5 p^2, \quad (14)$$

where γ are the usual Dirac matrices and p is the momentum operator.

The matrix element of scalar-pseudoscalar P,T-odd interaction constant, W_s , is given by

$$W_s = \frac{1}{\Omega k_s} \langle \Psi_\Omega | \sum_j^n H_{\text{SP}}(j) | \Psi_\Omega \rangle, \quad (15)$$

where, k_s is the dimension less electron-nucleus scalar-pseudoscalar coupling constant which is defined as $Zk_s = (Zk_{s,p} + Nk_{s,n})$, where $k_{s,p}$ and $k_{s,n}$ are electron-proton and electron-neutron coupling constant, respectively.

The interaction Hamiltonian is defined as [36]

$$H_{\text{SP}} = i \frac{G_F}{\sqrt{2}} Zk_s \gamma^0 \gamma^5 \rho_N(r), \quad (16)$$

where $\rho_N(r)$ is the nuclear charge density normalized to unity and G_F is the Fermi constant. The calculation of the above matrix elements depends on the accurate wavefunction in the core (near nuclear) region and the standard way to determine the accuracy of the electronic wavefunction in that region is to compare the theoretically calculated hyperfine structure (HFS) constant with

Hamiltonian with respect to external field of perturbation. The detailed diagrammatic expression is given in Fig. 2 and the corresponding algebraic equation is given in the following Eq. 12,

the experimental value. The magnetic hyperfine constant of the J^{th} electronic state of an atom is given by

$$A_J = \frac{\vec{\mu}_k}{IJ} \cdot \langle \Psi_J | \sum_i^n \left(\frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right) | \Psi_J \rangle, \quad (17)$$

where Ψ_J is the wavefunction of the J^{th} electronic state, I is the nuclear spin quantum number and $\vec{\mu}_k$ is the magnetic moment of the nucleus k . For a diatomic molecule, The parallel (A_{\parallel}) and perpendicular (A_{\perp}) magnetic hyperfine constant of a diatomic molecule can be written as

$$A_{\parallel(\perp)} = \frac{\vec{\mu}_k}{I\Omega} \cdot \langle \Psi_\Omega | \sum_i^n \left(\frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right)_{z(x/y)} | \Psi_{\Omega(-\Omega)} \rangle, \quad (18)$$

where the value of Ω is 1/2 for the ground electronic state ($^2\Sigma$) of RaF.

III. COMPUTATIONAL DETAILS

The locally modified version of DIRAC10 [37] program package is used to solve the DHF equation and to construct the one-body, two-body matrix elements and the one electron property integrals of interest. Finite size of nucleus with Gaussian charge distribution is considered as the nuclear model where the nuclear parameters [38] are taken as default values of DIRAC10. Small component basis functions are generated from the large component by applying restricted kinetic balance (RKB) [39] condition. The basis functions are represented in scalar basis and unphysical solutions are removed by means of the diagonalization of free particle Hamiltonian. This generates the electronic and positronic solution in 1:1 manner. In our calculations, we have used the following uncontracted basis sets: triple zeta (TZ) basis: dyall.cv3z [40] for Ra and cc-pCVTZ [41] for F; quadruple zeta (QZ) basis: dyall.cv4z [40] basis for Ra and cc-pCVQZ [41] basis for F. In TZ basis, three calculations are done for the magnetic HFS constant of Ra^+ by using 51, 69 and 87

TABLE I: Cutoff used and correlation energy of the ground state of Ra^+ and RaF in different basis sets

		Basis		Cutoff (a.u.)		Spinor		Correlation Energy (a.u.)	
Name	Nature	Ra	F	Occupied	Virtual	Occupied	Virtual	MBPT(2)	CCSD
Ra ⁺									
A	TZ	dyall.cv3z		-30	500	51	323	-1.74841495	-1.57235409
B	TZ	dyall.cv3z		-130	500	69	323	-2.42790147	-2.20700361
C	TZ	dyall.cv3z			500	87	323	-2.78897499	-2.55468917
D	QZ	dyall.cv4z		-30	20	51	349	-1.43221422	-1.31515023
E	QZ	dyall.cv4z		-130	20	69	349	-1.49747209	-1.37242346
F	QZ	dyall.cv4z			20	87	349	-1.50382815	-1.37827038
RaF									
G	TZ	dyall.cv3z	cc-pCVTZ	-30	500	61	415	-2.09671991	-1.91684123
H	TZ	dyall.cv3z	cc-pCVTZ	-130	500	79	415	-2.77624243	-2.55153111
I	TZ	dyall.cv3z	cc-pCVTZ		500	97	415	-3.13733209	-2.89923481
J	QZ	dyall.cv4z	cc-pCVQZ	-30	20	61	449	-1.76368821	-1.63988444
K	QZ	dyall.cv4z	cc-pCVQZ	-130	20	79	449	-1.82908547	-1.69728677
L	QZ	dyall.cv4z	cc-pCVQZ		20	97	449	-1.83544557	-1.70314714

number of correlated electrons and these are denoted by A, B and C, respectively. In QZ basis, three more calculations are done by using 51, 69 and 87 number of correlated electrons and these are denoted by D, E and F, respectively. The properties of RaF are calculated using two different basis. In TZ basis, three calculations are done by using 61, 79 and 97 correlated electrons and those are denoted by G, H and I, respectively and similarly in QZ basis, the calculations using 61, 79 and 97 correlated electrons are denoted by J, K and L, respectively. The bond length of RaF is taken as $4.23a_0$ (2.24 \AA) [31] in all our calculation.

IV. RESULTS AND DISCUSSION

The aim of the present study is to exploit RaF molecule for the eEDM experiment and to provide more accurate value of the P,T-odd interaction constants of RaF . Since, there are no experimental analogue of the P,T-odd interaction constants like E_{eff} and W_s , the accuracy of these theoretically obtained quantities can be assessed by comparing the theoretically obtained HFS values with the corresponding experimental values. Unfortunately, the experimental HFS results of Ra in RaF are not available.

TABLE II: Hyperfine coupling constant (in MHz) of $^{223}\text{Ra}^+$

Basis	Expectation	Z-vector	Expt. [42, 43]
A	3458	3418	3404(2)
B	3504	3464	
C	3547	3506	
D	3434	3394	
E	3448	3409	
F	3453	3414	

Therefore, we compare the experimental HFS value of $^{223}\text{Ra}^+$ [42, 43] with the value obtained by theory using the same basis of Ra as used for the calculation of RaF .

In Table I, we present the information regarding the employed basis-sets, cutoff used for occupied and virtual orbitals and the the number of active spinor for the correlation calculation. We also compiled the correlation energy obtained from second-order many-body perturbation theory (MBPT(2)) and CCSD method in the same table.

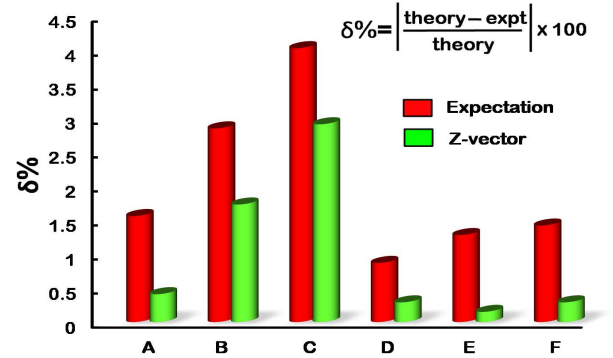


FIG. 3: Comparison of relative deviations between the results of expectation value and Z-vector method with experiment.

In Table II, we present the ground state (2S) magnetic HFS constant value of $^{223}\text{Ra}^+$ using both expectation value and Z-vector method. Our results are compared with the available experimental value [42, 43]. The deviations of Z-vector and expectation values from the experiment are presented in Fig. 3. It is clear that the deviations of expectation value method are always greater than those of Z-vector method. This is expected because Z-vector is a better method than the expectation value

method for the ground state property; in fact, the Z-vector value is the corresponding expectation value plus some additional terms which make it closer to the FCI property value. It is interesting to note that when we go from TZ to QZ basis with same number of correlated electrons (i.e., from A to D, B to E, and C to F), the relative deviation of both Z-vector and expectation value decreases. This is because QZ, in comparison to TZ, further improves the configuration space by adding one higher angular momentum basis function. It is also interesting to see that in TZ basis, if we go from A to B and B to C, the addition of 18 electrons (4s+3d+4p and 1s-3p) changes the Z-vector HFS constant by 46 MHz and 42 MHz. Similarly in QZ basis, as we go from D to E and E to F, the addition of 18 electrons changes the Z-vector HFS constant by 15 MHz and 5 MHz. From this observation, we can comment that the core polarization plays a definite role in the correlation contribution of HFS constant and the effect is severe for lower basis sets. Further, the enlargement of basis set and addition of core electrons have opposite effects in the calculated HFS value of Ra^+ . However, The magnetic HFS constant obtained in all electron Z-vector calculation using QZ basis (basis F) is very close to the experimental value ($\delta\% = 0.29$).

TABLE III: Molecular dipole moment (μ) and magnetic HFS constants of ^{223}Ra in RaF

Basis	μ (D)		A_{\perp} (MHz)		A_{\parallel} (MHz)	
	Expect.	Z-vector	Expect.	Z-vector	Expect.	Z-vector
G	3.7059	3.7220	2031	1987	2123	2078
H	3.7028	3.7207	2059	2014	2152	2107
I	3.7017	3.7201	2084	2038	2178	2132
J	3.8404	3.8474	2029	1982	2119	2072
K	3.8375	3.8459	2037	1991	2128	2082
L	3.8374	3.8459	2040	1993	2131	2085

The properties described by Eqs. 13, 15 and 18 strongly depend on the electronic configuration of the given (heavy) atom and are also known as “atom in compound (AIC)” properties [44]. The accuracy of the theoretically calculated AIC properties depends on the accurate evaluation of the electron density near the atomic core region. From the accuracy of our calculated HFS constant of Ra^+ ($\delta\% = 0.29$), we can comment that the all electron Z-vector calculation produces an accurate wavefunction in the vicinity of Ra nucleus and we also expect the same kind of accuracy for RaF molecule.

We have calculated the molecular-frame dipole moment (μ) of RaF, perpendicular (A_{\perp}) and parallel (A_{\parallel}) magnetic HFS constants of ^{223}Ra in RaF using both expectation value and Z-vector method. The results are compiled in Table III. From this table, it is clear that inclusion of more core electrons decreases the value of μ but increases the value of magnetic HFS constants of ^{223}Ra in RaF. On the other hand, if we go from TZ to QZ ba-

sis, the μ value is increased but the magnetic HFS values are decreased. This observation shows that the increase of correlation space either by the addition of core electrons or higher angular momentum wavefunctions have opposite effect on the near nuclear and outer region part of the molecular wavefunction of RaF. We can also comment that the enlargement of basis set and core electrons have opposite effects in the properties of RaF.

TABLE IV: P,T-odd interaction constants and their ratio of RaF

Basis	W_s (kHz)		E_{eff} (GV/cm)		R ($10^{18}/e$ cm)	
	Expect.	Z-vector	Expect.	Z-vector	Expect.	Z-vector
G	144.7	143.6	53.9	53.5	90.1	90.1
H	147.4	146.3	54.9	54.5	90.1	90.1
I	149.3	148.1	55.6	55.1	90.0	90.0
J	141.2	140.4	52.6	52.3	90.1	90.1
K	141.9	141.1	52.8	52.5	90.0	90.0
L	142.0	141.2	52.8	52.5	89.9	89.9

In Table IV, we present the two P,T-odd interaction constant, namely E_{eff} and W_s . The E_{eff} value of RaF in QZ basis using all electron Z-vector calculation (basis L) is 52.5 GV/cm. This E_{eff} value of RaF is even higher than the E_{eff} value of YbF in its ground state [45–50]. The W_s value of RaF using Z-vector method in the same basis (QZ, all electron) is 141.2 kHz. This high value of W_s suggests that the S-PS interaction will also be responsible for significant change in the P,T-odd frequency shift in the eEDM experiment. These results reveal the possibility of using RaF in future eEDM experiment. The ratio (R) of E_{eff} to W_s is also calculated as this is a very important quantity to obtain the independent limit of d_e and k_s by using two independent experiments. Our calculated value of R using all electron Z-vector method in QZ (L) basis is 89.9 in units of $10^{18}/e$ cm. Using this ratio, the relation of independent d_e and k_s with experimentally determined d_e^{expt} becomes (for more details see Ref. [51])

$$d_e + 5.56 \times 10^{-21} k_s = d_e^{\text{expt}}|_{k_s=0}, \quad (19)$$

where $d_e^{\text{expt}}|_{k_s=0}$ is the eEDM limit derived from the experimentally measured P,T-odd frequency shift at the limit $k_s = 0$.

We have compared our calculated results with other theoretically obtained values in table V. The first *ab initio* calculation of W_s of RaF was performed by Isaev *et al.* [30]. They employed two-component zeroth-order regular approximation (ZORA) generalized Hartree-Fock (GHF) method and obtained the value of W_s as 150 kHz. They also obtained the value of E_{eff} as 45.5 GV/cm by using ZORA-GHF value of W_s and the approximate ratio between E_{eff} and W_s . Kudashov *et al.* [31] employed two different methods to incorporate relativistic and electron correlation effects: (i) spin-orbit direct con-

TABLE V: Comparison of magnetic HFS constant (^{223}Ra), W_s and E_{eff} of RaF

Method	A_{\perp} (MHz)	A_{\parallel} (MHz)	W_s kHz	E_{eff} (GV/cm)
ZORA-GHF [30]	1860	1900	150	45.5
SODCI [31]	1720	1790	131	49.6
FS-RCC [31]	2020	2110	139	52.9
This work (QZ basis, all electron)				
Expect.	2040	2131	142.0	52.8
Z-vector	1993	2085	141.2	52.5

figuration interaction (SODCI) method and (ii) relativistic two-component Fock-space coupled cluster approach (FS-RCC) within single- and double- excitation approximation. However, it is worth to remember that truncated CI is not size extensive and thus cannot treat electron correlation properly, specially, for the heavy electronic system like RaF where the number of electron is so large. In their FS-RCC method, Kudashov *et al.* [31] calculated the properties of RaF using the finite field method, which is a numerical technique. They corrected the error associated with their calculation considering higher order correlation effect and basis set with the addition of partial triple in the CCSD model (CCSD(T)) and using enlarged basis set, respectively. They have done those corrections only for the ground state ((0,0) sector of Fock space) coupled cluster amplitudes. On the other hand, we have calculated the property values of RaF via two analytical methods (expectation value and Z-vector method)

in the relativistic coupled-cluster framework within four-component formalism. We also calculated the E_{eff} and W_s values directly by using Eqs. 13 and 15, respectively.

V. CONCLUSION

In conclusion, we have applied both Z-vector and expectation value method in the relativistic coupled-cluster framework to calculate parallel and perpendicular magnetic HFS constant of ^{223}Ra in RaF, E_{eff} and W_s of RaF. We have also calculated the magnetic HFS constant of $^{223}\text{Ra}^+$ to show the reliability of our results. Our most reliable value of E_{eff} and W_s of RaF are 52.5 GV/cm and 141.2 kHz, respectively. This shows that RaF can be a potential candidate for eEDM experiment. We also showed that core electrons play significant role and the effect is notable for lower basis sets. Our results also show that the Z-vector, being an energy derivative method, is much more reliable than the expectation value method.

Acknowledgement

Authors acknowledge a grant from CSIR 12th Five Year Plan project on Multi-Scale Simulations of Material (MSM) and the resources of the Center of Excellence in Scientific Computing at CSIR-NCL. S.S. and H.P acknowledge the CSIR for their fellowship. S.P. acknowledges funding from J. C. Bose Fellowship grant of Department of Science and Technology (India).

-
- [1] J. Ginges and V. Flambaum, *Physics Reports* **397**, 63 (2004).
 - [2] P. Sandars, *Physics Letters* **14**, 194 (1965).
 - [3] P. G. H. Sandars, *Phys. Rev. Lett.* **19**, 1396 (1967).
 - [4] L. N. Labzovskii, *Sov. Phys. JETP* **48**, 434 (1978).
 - [5] L. M. Barkov, M. S. Zolotarev, and I. B. Khriplovich, *Soviet Physics Uspekhi* **23**, 713 (1980).
 - [6] F. L. Shapiro, *Soviet Physics Uspekhi* **11**, 345 (1968).
 - [7] M. Pospelov and A. Ritz, *Annals of physics* **318**, 119 (2005).
 - [8] W. Bernreuther and M. Suzuki, *Rev. Mod. Phys.* **63**, 313 (1991).
 - [9] B. C. Regan, E. D. Commins, C. J. Schmidt, and D. DeMille, *Phys. Rev. Lett.* **88**, 071805 (2002).
 - [10] J. Hudson *et al.*, *Nature* **473**, 493 (2011).
 - [11] J. Baron *et al.*, *Science* **343**, 269 (2014).
 - [12] I. B. Khriplovich and S. K. Lamoreaux, *CP Violation without Strangeness: The Electric Dipole Moments of Particles, Atoms, and Molecules* (Springer, London, 2011).
 - [13] E. D. Commins, *Advances In Atomic, Molecular, and Optical Physics* **40**, 1 (1999).
 - [14] O. Sushkov and V. Flambaum, *Journal of Experimental and Theoretical Physics* **48**, 608 (1978).
 - [15] V. V. Flambaum, *Sov. J. Nucl. Phys.* **24**, 199 (1976).
 - [16] V. A. Dzuba, V. V. Flambaum, and C. Harabati, *Phys. Rev. A* **84**, 052108 (2011).
 - [17] H. J. Monkhorst, *Int. J. Quantum Chem.* **12**, 421 (1977).
 - [18] N. C. Handy and H. F. Schaefer, *The Journal of Chemical Physics* **81**, 5031 (1984).
 - [19] E. A. Salter, G. W. Trucks, and R. J. Bartlett, *The Journal of Chemical Physics* **90**, 1752 (1989).
 - [20] H. Koch *et al.*, *The Journal of Chemical Physics* **92**, 4924 (1990).
 - [21] R. J. Bartlett and J. Noga, *Chemical physics letters* **150**, 29 (1988).
 - [22] R. J. Bartlett, S. A. Kucharski, and J. Noga, *Chemical physics letters* **155**, 133 (1989).
 - [23] J. Arponen, *Annals of Physics* **151**, 311 (1983).
 - [24] R. Bishop, J. Arponen, and P. Pajanne, *Aspects of Many-body Effects in Molecules and Extended Systems* (Springer-Verlag, Berlin, 1989).
 - [25] P. G. Szalay, M. Nooijen, and R. J. Bartlett, *The Journal of Chemical Physics* **103**, 281 (1995).
 - [26] C. Sur, R. K. Chaudhuri, B. K. Sahoo, B. P. Das, and D. Mukherjee, *Journal of Physics B: Atomic, Molecular and Optical Physics* **41**, 065001 (2008).
 - [27] C. Sur and R. K. Chaudhuri, *Phys. Rev. A* **76**, 032503

- (2007).
- [28] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, *Phys. Rev. A* **91**, 022512 (2015).
 - [29] T. A. Isaev, S. Hoekstra, and R. Berger, *Phys. Rev. A* **82**, 052521 (2010).
 - [30] T. Isaev and R. Berger, arXiv preprint arXiv:1302.5682 (2013).
 - [31] A. D. Kudashov *et al.*, *Phys. Rev. A* **90**, 052513 (2014).
 - [32] J. Cizek, *Advances in Chemical Physics: Correlation Effects in Atoms and Molecules* (Wiley, Hoboken, NJ, 1967).
 - [33] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, *Phys. Rev. A* **91**, 030503 (2015).
 - [34] M. G. Kozlov, V. Fomichev, Y. Y. Dmitriev, L. N. Labzovsky, and A. V. Titov, *Journal of Physics B: Atomic and Molecular Physics* **20**, 4939 (1987).
 - [35] A. V. Titov, N. S. Mosyagin, A. N. Petrov, T. A. Isaev, and D. P. DeMille, *Progr. Theor. Chem. Phys.* **15**, 253 (2006).
 - [36] L. R. Hunter, *Science* **252**, 73 (1991).
 - [37] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC10 (2010), written by T. Saue, L. Visscher and H. J. Aa. Jensen, with contributions from R. Bast, K. G. Dyall, U. Ekström, E. Eliav, T. Enevoldsen, T. Fleig, A. S. P. Gomes, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, H. S. Nataraj, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, B. Schimmelpfennig, J. Sikkema, A. Thorvaldsen, J. Thyssen, S. Villaume, and S. Yamamoto (see <http://www.diracprogram.org>).
 - [38] L. Visscher and K. Dyall, *Atomic Data and Nuclear Data Tables* **67**, 207 (1997).
 - [39] K. Faegri Jr and K. G. Dyall, *Introduction to relativistic quantum chemistry* (Oxford University Press, USA, 2007).
 - [40] K. G. Dyall, *The Journal of Physical Chemistry A* **113**, 12638 (2009).
 - [41] T. H. Dunning, *The Journal of Chemical Physics* **90**, 1007 (1989).
 - [42] K. Wendt *et al.*, *Zeitschrift für Physik D Atoms, Molecules and Clusters* **4**, 227 (1987).
 - [43] W. Neu *et al.*, *Zeitschrift für Physik D Atoms, Molecules and Clusters* **11**, 105 (1989).
 - [44] A. V. Titov, Y. V. Lomachuk, and L. V. Skripnikov, *Phys. Rev. A* **90**, 052522 (2014).
 - [45] M. G. Kozlov and V. F. Ezhov, *Phys. Rev. A* **49**, 4502 (1994).
 - [46] M. Kozlov, *Journal of Physics B: Atomic, Molecular and Optical Physics* **30**, L607 (1997).
 - [47] A. V. Titov, N. S. Mosyagin, and V. F. Ezhov, *Phys. Rev. Lett.* **77**, 5346 (1996).
 - [48] H. Quiney, H. Skaane, and I. Grant, *Journal of Physics B: Atomic, Molecular and Optical Physics* **31**, L85 (1998).
 - [49] F. A. Parpia, *Journal of Physics B: Atomic, Molecular and Optical Physics* **31**, 1409 (1998).
 - [50] N. Mosyagin, M. Kozlov, and A. Titov, *Journal of Physics B: Atomic, Molecular and Optical Physics* **31**, L763 (1998).
 - [51] S. Sasmal, H. Pathak, M. K. Nayak, N. Vaval, and S. Pal, arXiv preprint arXiv:1511.09218 (2015).